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# Modeling solubility of $CO_2$ and $C_2H_6$ mixtures in crosslinked poly(ethylene oxide) copolymers

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The evaluation of the mixed gas solubility in polymers is of fundamental importance for the development gas separation membranes [1-2]. The case of rubbery system can be conveniently described by an equation of state (EoS) model, that written in its multicomponent version, can be applied to calculate multiple gas solubility in the equilibrium phases. The use of an equation of state allows for a wide and accurate description of the physical properties of the system and gives the possibility of extrapolating the results in a much larger range of temperatures, pressures and compositions.

The present work is focused on the characterization of the sorption properties of gaseous mixtures of $CO_2$ and $C_2H_6$ in a crosslinked poly(ethylene oxide) copolymer, XLPEO, in a wide range of temperatures from a modeling point of view, by the use of Sanchez Lacombe EoS [3].

The polymer was prepared by photopolymerization of a solution containing 70 wt % poly(ethylene glycol) methyl ether acrylate (PEGMEA) and 30 wt % poly(ethylene glycol) diacrylate (PEGDA), as described in detail in ref [4,5] and the sorption experiments were performed by the barometric pressure-decay method [6] from -20°C up to 35°C.

The Sanchez Lacombe EoS needs three characteristic parameters for every substance in order to describe the properties of the pure components. Whereas the values of T*, p* and □* for $CO_2$ and $C_2H_6$ are already accessible from the literature, those of the polymer have to be calculated. To this aim, the experimental thermal expansion of the XLPEO copolymer between -20 and 35°C [4] is employed to calculate T* and □*. The calculation of the third parameter from pure polymer properties would require the isothermal compressibility which is not available from experiments, and therefore p* was taken as equal to that of pure poly(ethylene oxide) as calculated from pVT data reported by Zoller and Walsh [7].

The analysis of the pure component sorption in XLPEO was performed by means of the Sanchez Lacombe EoS for the optimization of the binary interaction coefficients polymer/penetrant to account for their deviation from ideality of energetic interactions. Considering rather small values of $k_{ij}$, 0.017 and 0.034 for $CO_2$ and $C_2H_6$, respectively, it was possible to have a very good agreement between experimental data and model predictions at all the values of temperature inspected, namely -20, -10, 0, 25 and 35°C. Furthermore, since the mixture of the two gases surely deviates from ideality, a non zero value of the binary coefficient between the two penetrants was taken, from the best fitting of vapor liquid equilibrium data a value of $k_{ij}$ equal to 0.08 was retrieved [8].

In Figure 1, the solubility of $CO_2$ in XLPEO at all the temperatures is reported together with the model predictions given by the Sanchez-Lacombe EoS.



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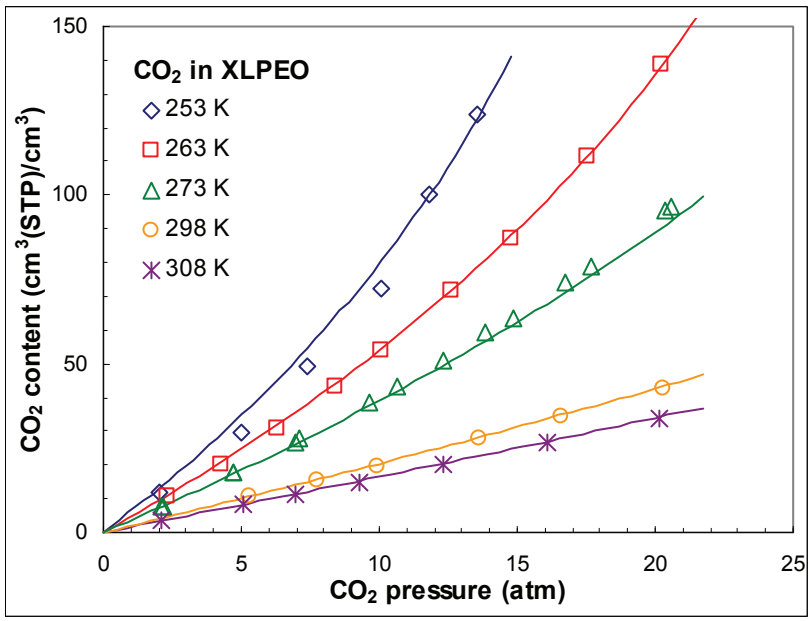


**Figure 1**, $CO_2$ sorption isotherms in XLPEO at -20, -10, 0, 25 and 35°C, experimental data from ref. [4,5] and model prediction with Sanchez Lacombe EoS considering $k_{ij}$=0.017.

As one can see, the agreement between experimental data and model predictions is remarkable. Analogous behaviors of the sorption isotherms and the same ability of the model to predict the experimental trends was found also for pure ethane as penetrant at all temperature values inspected.

As already mentioned, the analysis of the three binary systems allowed the determination of the three binary interaction parameters which where then used to describe the ternary system.

The multicomponent sorption was investigated at the temperature values above mentioned and in a wide range of concentrations $CO_2/C_2H_6$: 10/90, 25/75 50/50 and 75/25.

Figure 2 illustrates that Sanchez-Lacombe EoS, in its multicomponent version, is able to describe the sorption of a gaseous mixture in a crosslinked PEO membrane. The results of sorption of a 50/50 $CO_2/C_2H_6$ mixture in XLPEO at all temperatures are reported in terms of concentration of the two gases in the polymer as function of the partial pressure of the respective gases.

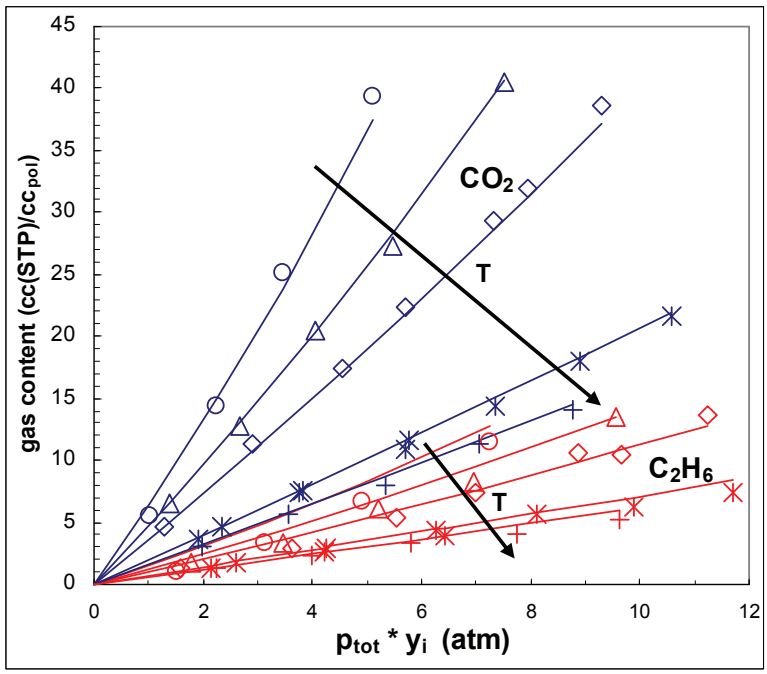


**Figure 2**, $CO_2$ and $C_2H_6$ sorption isotherms in XLPEO at -20, -10, 0, 25 and 35°C, for a 50/50 gaseous mixtures. Experimental data from ref. [4,5] and model prediction with Sanchez Lacombe EoS.

Whereas experimental results and model predictions are very close at the highest temperatures, at -10 and -20°C the agreement is poorer, especially for the gaseous mixtures richer in ethane. However average deviations never exceed 20%. In these cases, the model tends to overestimate the ethane solubility in XLPEO, and correctly evaluates the corresponding value of $CO_2$.

Once the Sanchez-Lacombe was proved to be accurate for the description of this system, the model allowed then the prediction of mixed gas solubility selectivity factor ($S_{CO2}/S_{C2H6}$) for real mixtures in different conditions, for instance, at various temperatures, compositions and pressure values. In particular, it is observed that the $CO_2$ and $C_2H_6$ uptake in the polymers can be significantly affected by the presence of the other gas, showing different trends depending on temperature composition and pressure.

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